

Supporting Information

Hydrodehalogenation of aryl halides catalyzed by cost-effective
bimetallic nanoparticles under mild conditions

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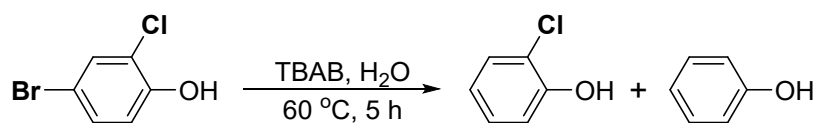
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1. Catalyst Characterization and optimization experiments:

Table S1 elemental composition of the catalysts

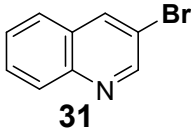
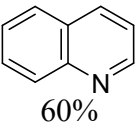
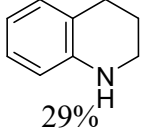
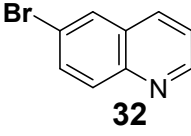
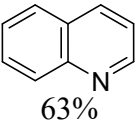
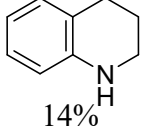
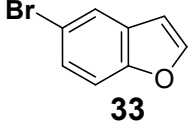
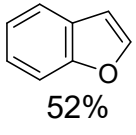
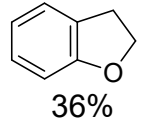
Sample	Ni (wt%)	Ag (wt%)	Molar ratio
Fresh	90.2	7.8	95.5:4.5
After 5 cycles	81.5	7.5	95.2:4.8

Table S2 Screening of the catalysts

Entry	T/°C	Yield/%	
		2-CP	Phenol
1	Fe	6	-
2	Cu	1	-
3	Co	28	12
4	Ni	33	65
5	Ni ₉₀ Fe ₁₀	51	36
6	Ni ₉₀ Co ₁₀	44	49
7	Ni ₉₀ Cu ₁₀	53	42
8	Ni _{97.5} Ag _{2.5}	19	80
9	Ni ₉₅ Ag ₅	-	99
10	Ni ₉₀ Ag ₁₀	5	94
11	Ni ₈₀ Ag ₂₀	19	76
12	Ag	57	5
13	SDBS	-	-

Reaction conditions: 4-bromo-2-chlorophenol (1 mmol), catalyst (50 mg), H₂O (3 mL), TBAB 1 equiv, 60 °C for 5 h. Yield determined by GC.

Table S3 Products of Substrate 31-33 without adding K₃PO₄

Substrate	Product 1	Product 2
 31	 60%	 29%
 32	 63%	 14%
 33	 52%	 36%

Reaction conditions: Substrate 31-33 (1 mmol), Ni₉₅Ag₅ (50 mg), H₂O (3 mL), TBAB 1 equiv, 60 °C for 10-12 h. Yield determined by GC.

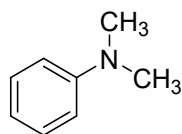
Figure S1 $^1\text{H-NMR}$ of the product phenol use H_2O and D_2O as solvent

H_2O

D_2O

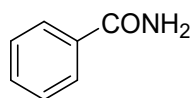
2. Characterization data of products:

N,N-Dimethylaniline



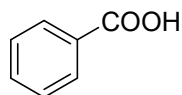
$^1\text{H-NMR}$ (500 MHz, CD_3CN): δ 7.26-7.21 (m, 2H), 6.80-6.77 (d, 2H), 6.72-6.68 (t, 1H), 2.93 (s, 6H); $^{13}\text{C-NMR}$ (125 MHz, CD_3CN): δ 151.0, 128.9, 116.3, 112.5, 39.8.

Benzamide



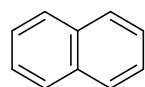
$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.86 (d, $J = 8.1$ Hz, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.49 (t, $J = 7.4$ Hz, 2H), 6.25 (br, 2H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 169.7, 130.0, 132.3, 128.7, 127.5.

Benzoic acid



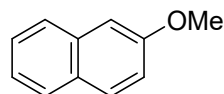
$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.18 (d, $J = 7.5$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 2H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 172.4, 133.9, 130.3, 129.3, 128.5.

Naphthalene



$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.92-7.89 (m, 4H), 7.55-7.52 (m, 4H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 133.5, 127.9, 125.7.

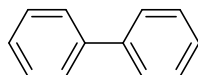
2-Methoxynaphthalene



$^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.84-7.79 (m, 3H), 7.51 (ddd, $J = 8.2, 6.9, 1.4$ Hz, 1H), 7.39 (ddd, $J = 8.0, 6.9, 1.2$ Hz, 1H), 7.23-7.20 (m, 2H), 3.98 (s, 3H); $^{13}\text{C-NMR}$

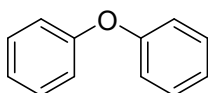
(125 MHz, CDCl₃): δ 157.6, 134.6, 129.4, 129.0, 127.7, 126.8, 126.4, 123.6, 118.8, 105.8, 55.3. The obtained spectroscopic data were in agreement with the reported data for this compound¹.

Biphenyl



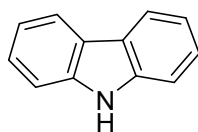
¹H-NMR (500 MHz, CDCl₃): δ 7.67-7.65 (m, 4H), 7.52-7.49 (m, 4H), 7.43-7.39 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃): δ 141.3, 128.8, 127.3, 127.2.

Diphenyl ether



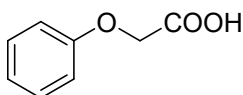
¹H-NMR (500 MHz, CDCl₃): δ 7.39 (t, J = 8.0 Hz, 4H), 7.16 (t, J = 7.4 Hz, 2H), 7.07 (t, J = 7.8 Hz, 4H); ¹³C-NMR (125 MHz, CDCl₃): δ 157.3, 129.8, 123.3, 118.9.

Carbazole



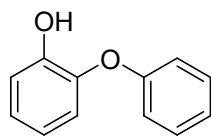
¹H-NMR (500 MHz, DMSO-*d*₆): δ 11.26 (s, 1H), 8.11 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.39 (ddd, J = 8.2, 7.0, 1.2 Hz, 2H), 7.16 (ddd, J = 7.9, 7.0, 1.1 Hz, 2H); ¹³C-NMR (125 MHz, DMSO-*d*₆): δ 140.2, 126.0, 122.8, 120.6, 118.9, 111.4. The obtained spectroscopic data were in agreement with the reported data for this compound².

Phenoxyacetic acid



¹H-NMR (500 MHz, CDCl₃): δ 7.36 (t, J = 8.0 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 4.73 (s, 2H); ¹³C-NMR (125 MHz, CDCl₃): δ 172.50, 157.33, 129.75, 122.21, 114.68, 64.84. The obtained spectroscopic data were in agreement with the reported data for this compound³.

2-Phenoxyphenol



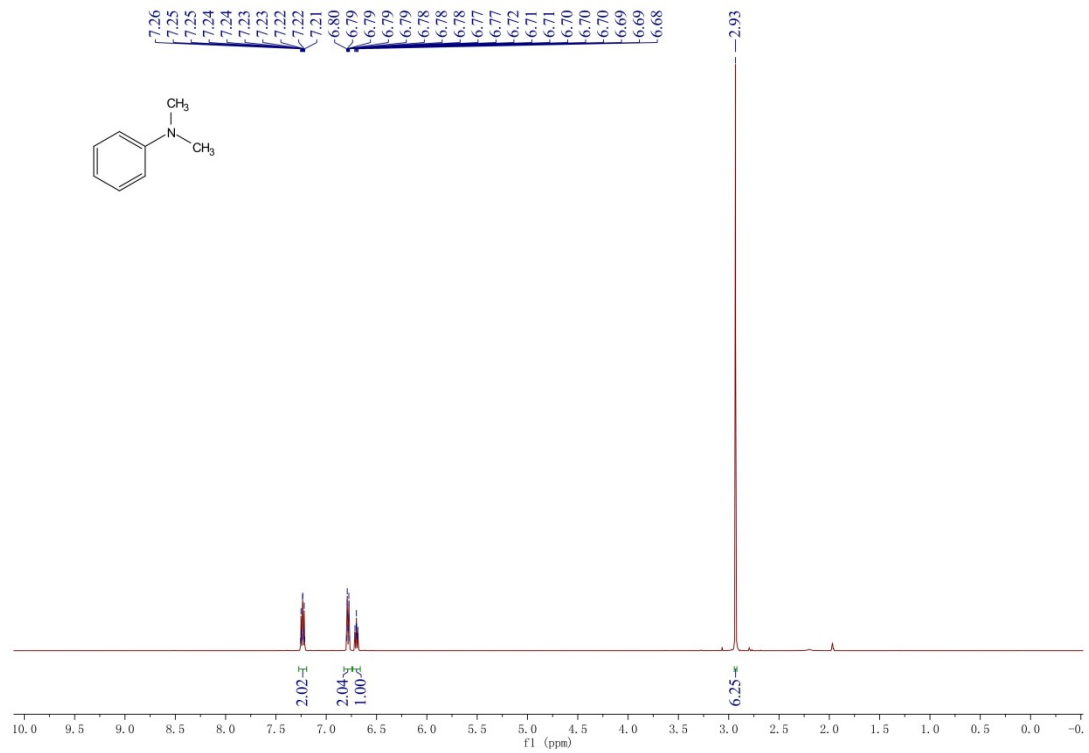
¹H-NMR (500 MHz, CDCl₃): δ 7.39 (t, 8.0 Hz, 2H), 7.17 (t, 7.4 Hz, 1H), 7.10-7.06 (m, 4H), 6.94-6.87 (m, 2H), 5.61 (s, 1H); ¹³C-NMR (125 MHz, CDCl₃): δ 156.8, 147.5, 143.5, 129.9, 124.8, 123.6, 120.7, 118.9, 118.0, 116.2. The obtained spectroscopic data were in agreement with the reported data for this compound⁴.

Reference:

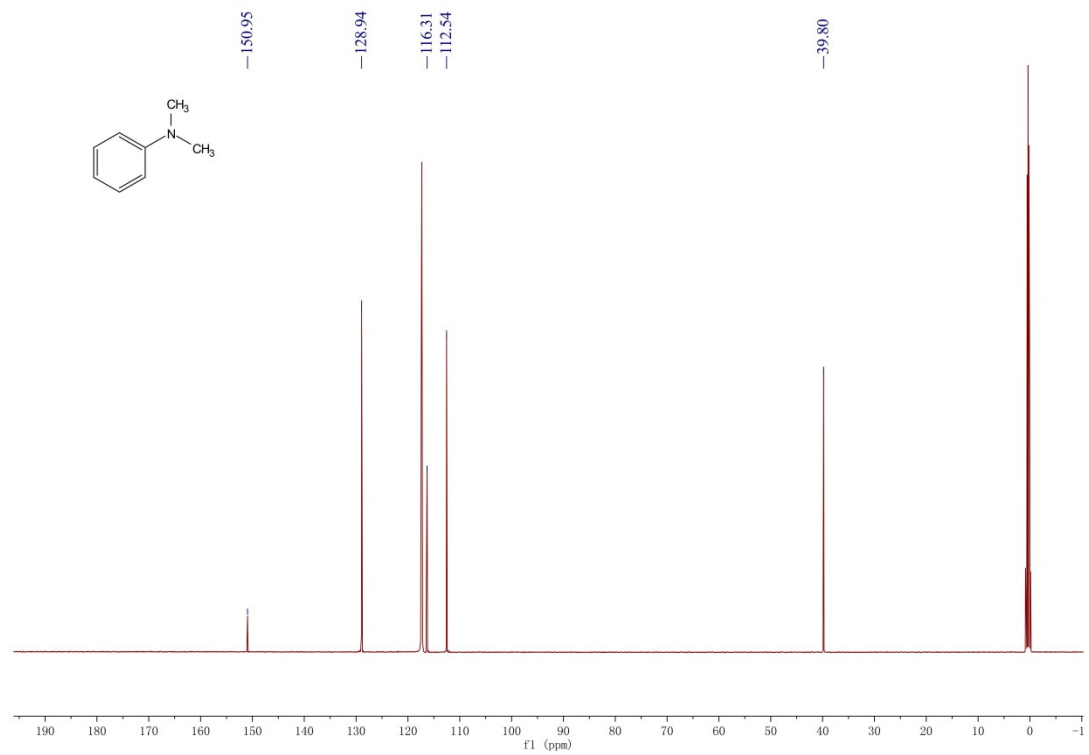
1. D. Y. Ong, C. Tejo, K. Xu, H. Hirao and S. Chiba, *Angew. Chem. Int. Ed.*, 2017, **56**, 1840-1844.
2. T. V. Nykaza, A. Ramirez, T. S. Harrison, M. R. Luzung and A. T. Radosevich, *J. Am. Chem. Soc.*, 2018, **140**, 3103-3113.
3. M. Rafiee, M. Alherech, S. D. Karlen and S. S. Stahl, *J Am Chem Soc*, 2019, **141**, 15266-15276.
4. W. Li, G. L. Gao, Y. Gao, C. Yang and W. J. Xia, *Chem. Commun.*, 2017, **53**, 5291.

Spectra of N, N-Dimethylaniline

¹H-NMR

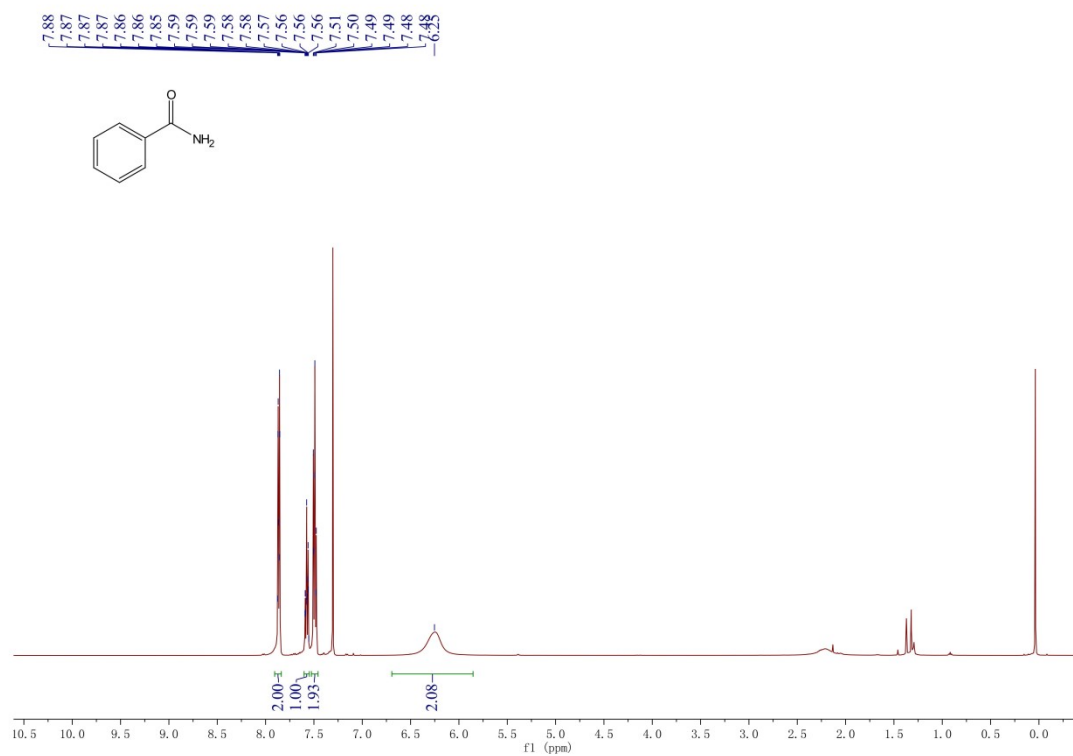


¹³C-NMR

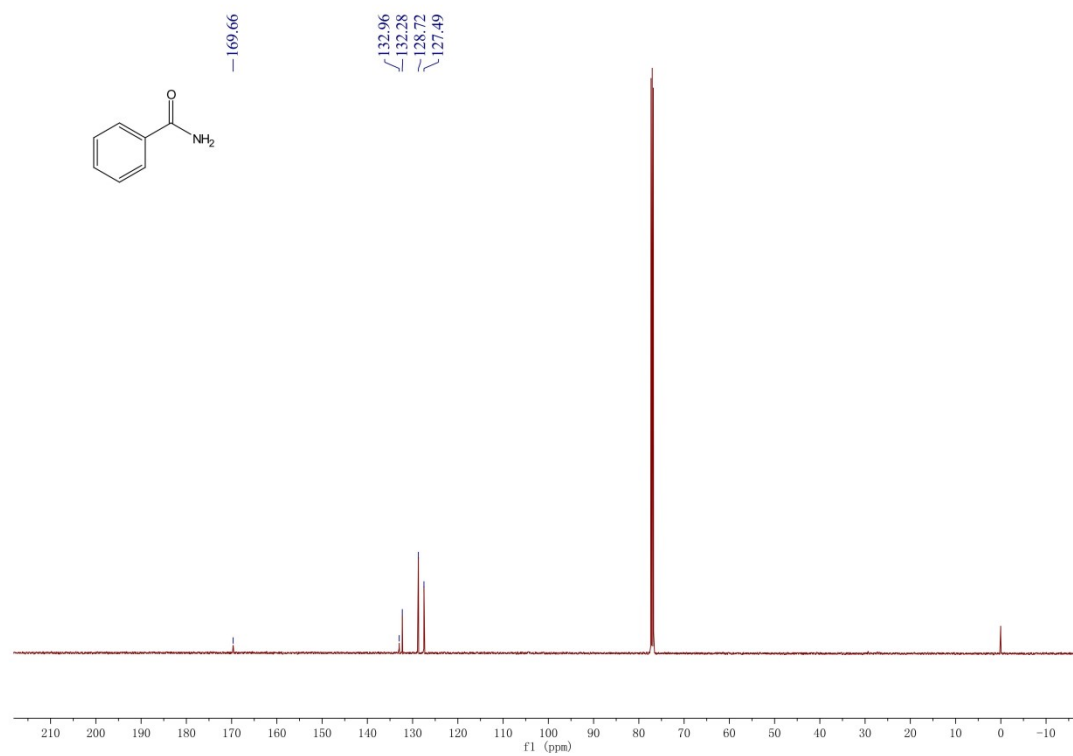


Spectra of Benzamide

¹H-NMR

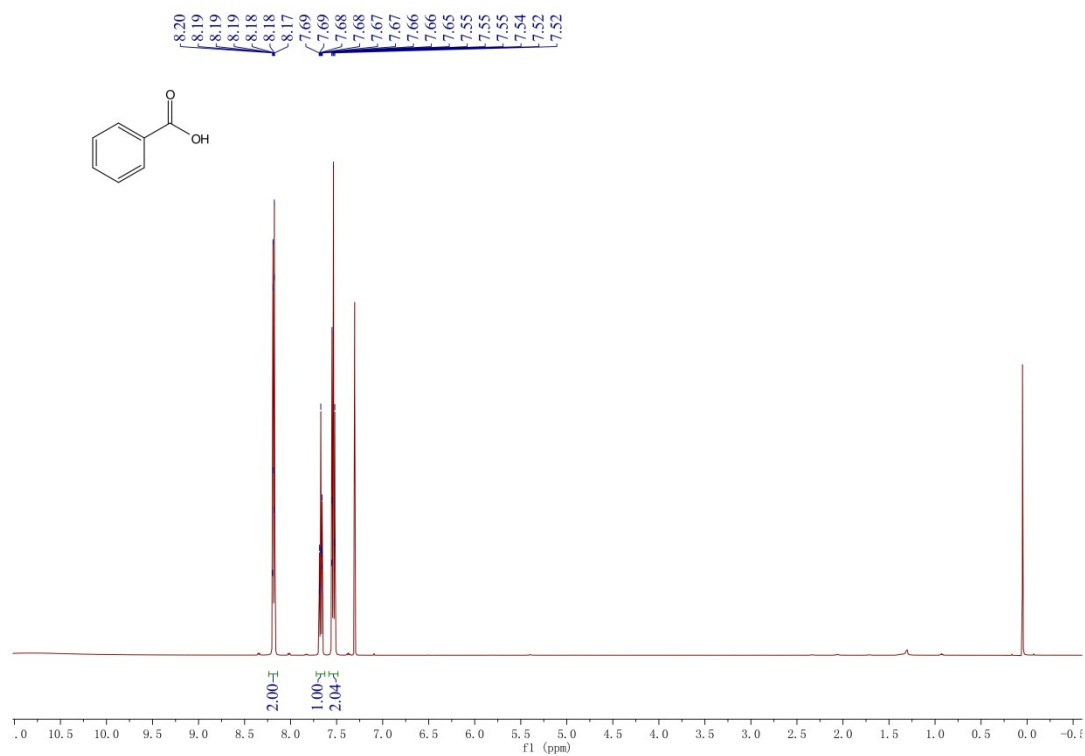


¹³C-NMR

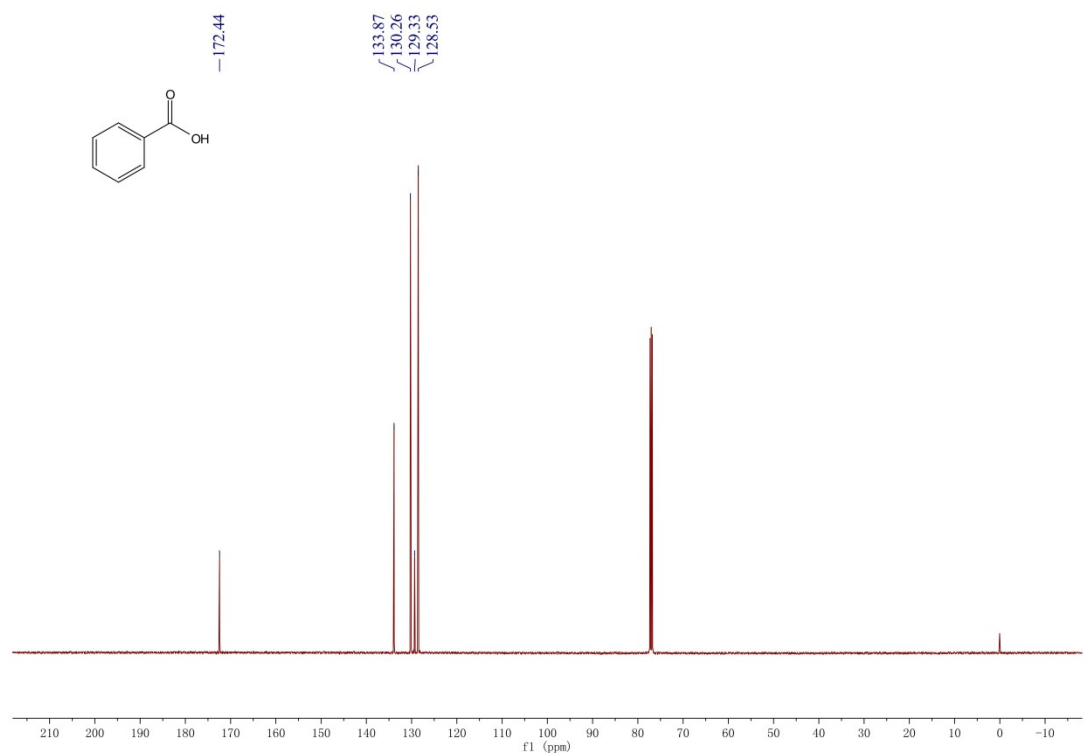


Spectra of Benzoic acid

¹H-NMR

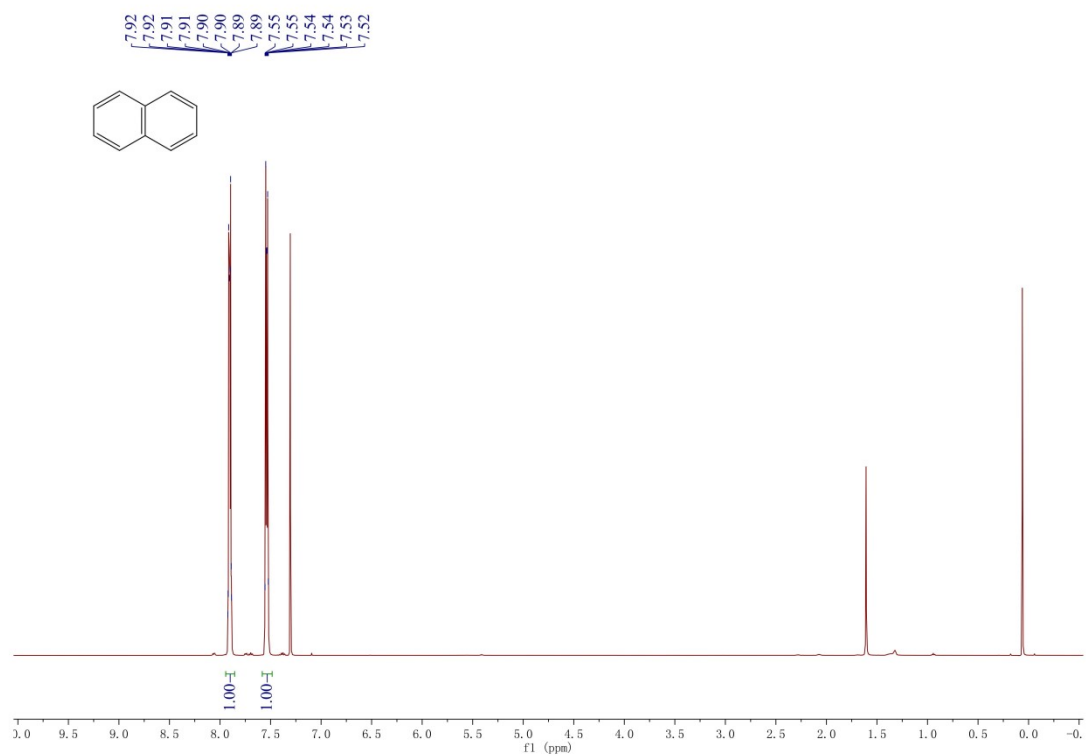


¹³C-NMR

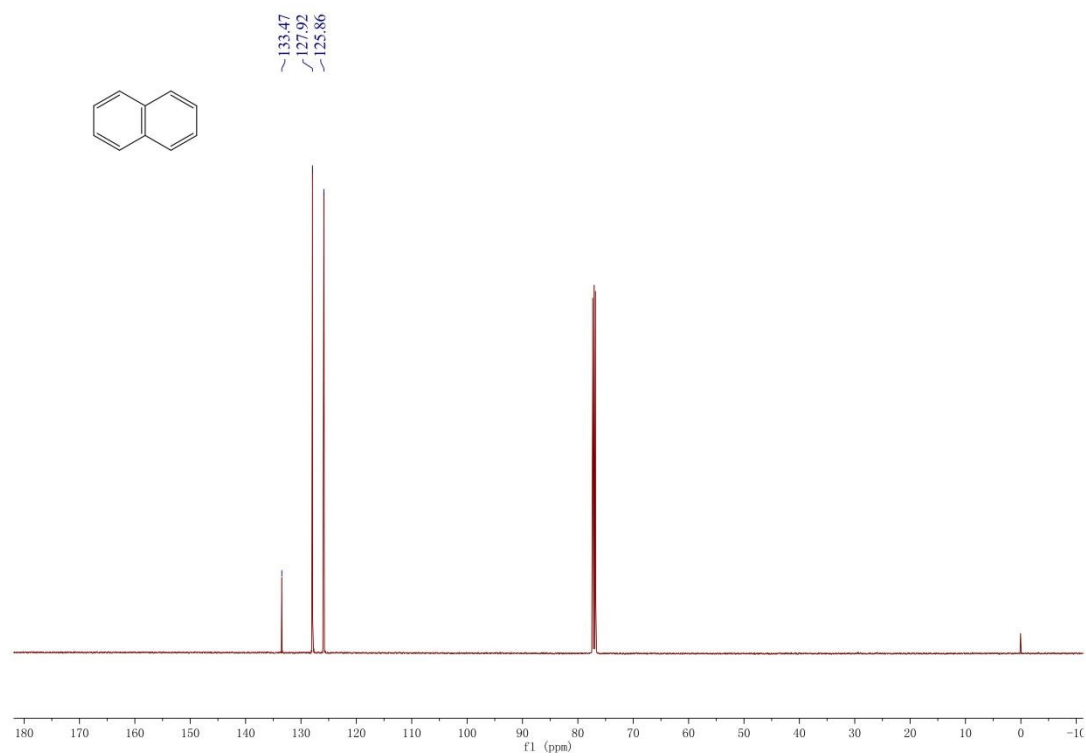


Spectra of Naphthalene

$^1\text{H-NMR}$

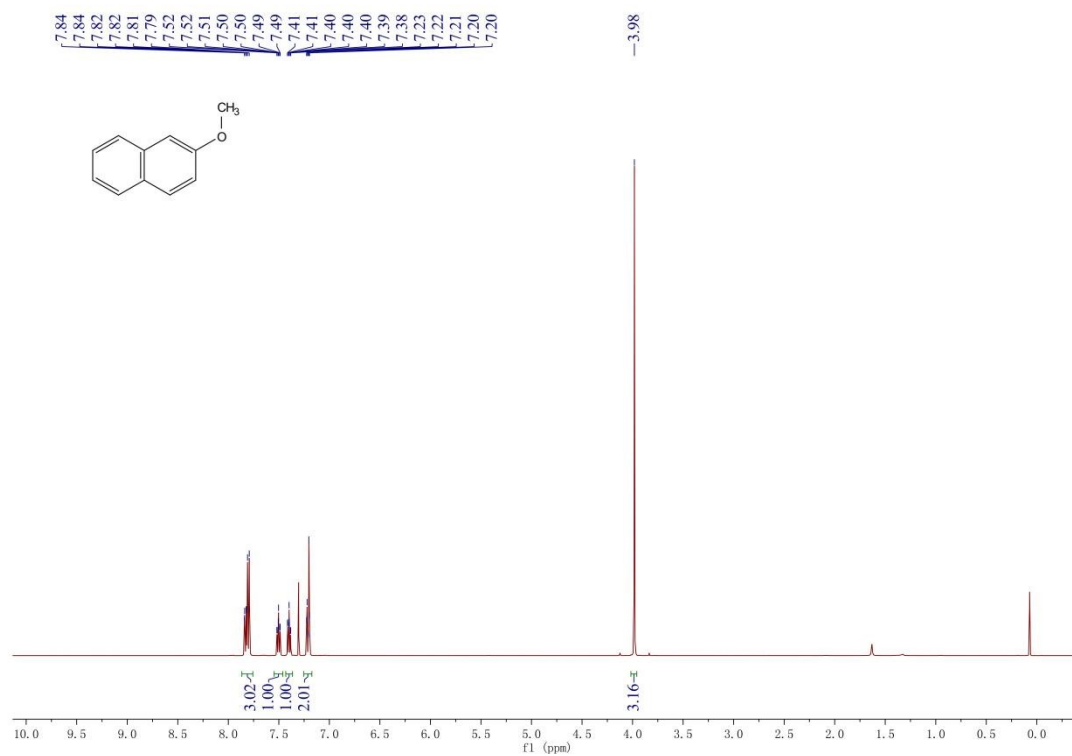


$^{13}\text{C-NMR}$

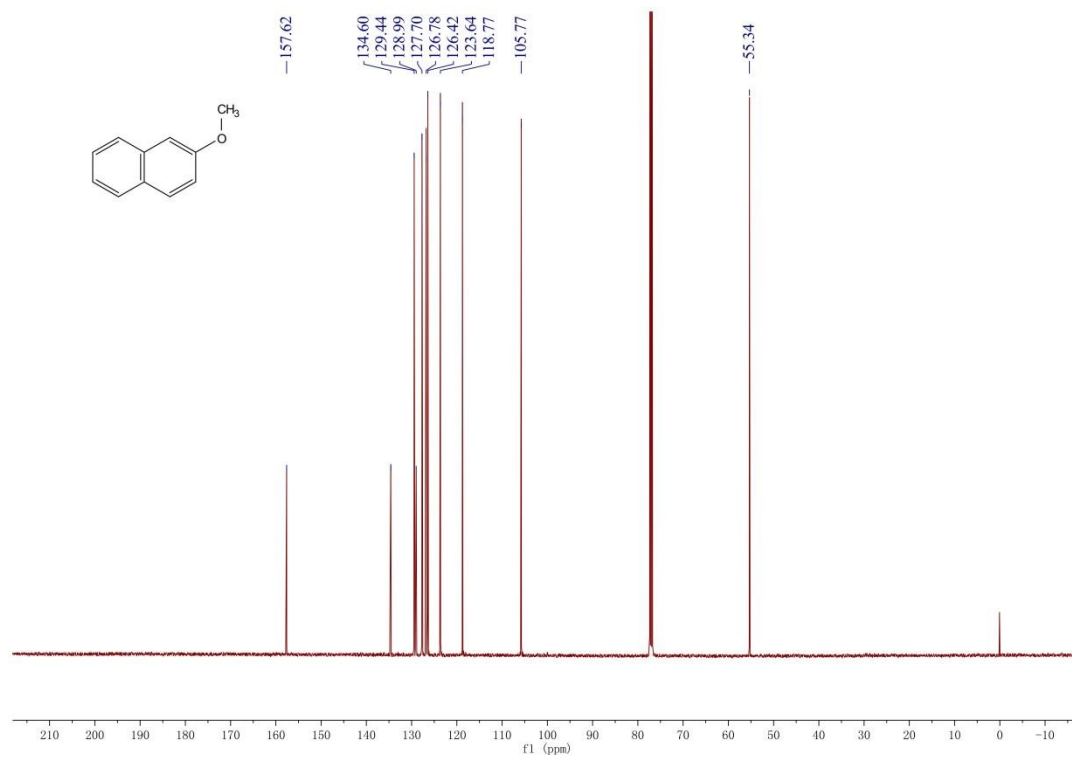


Spectra of 2-Methoxynaphthalene

$^1\text{H-NMR}$

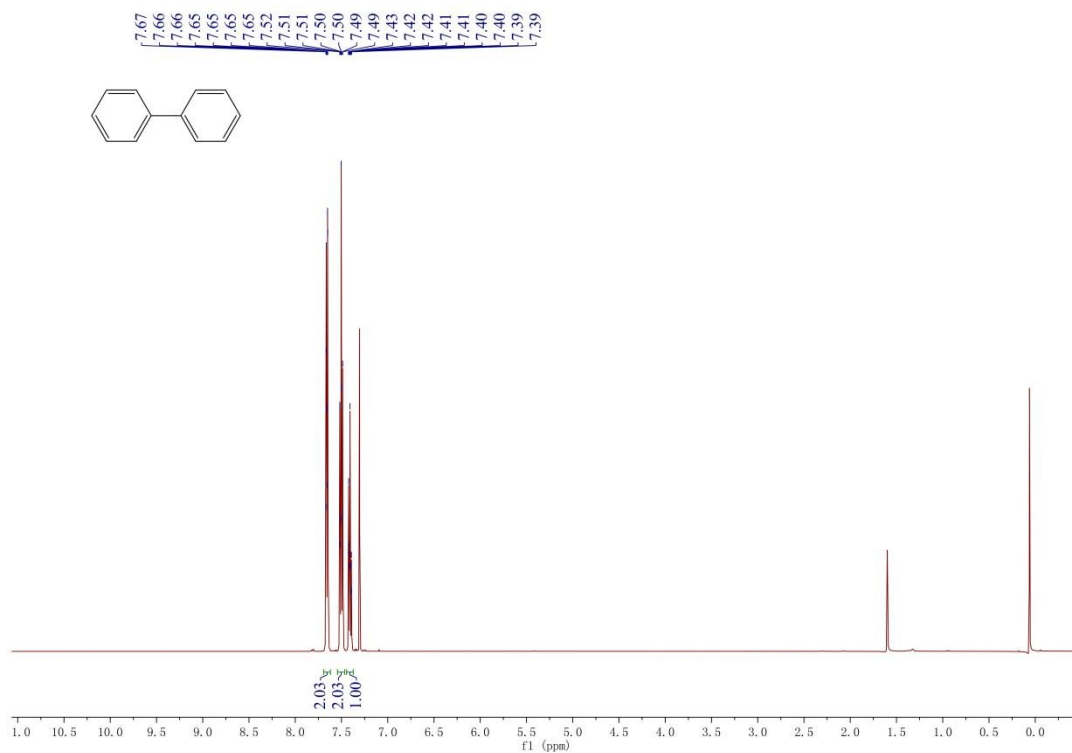


$^{13}\text{C-NMR}$

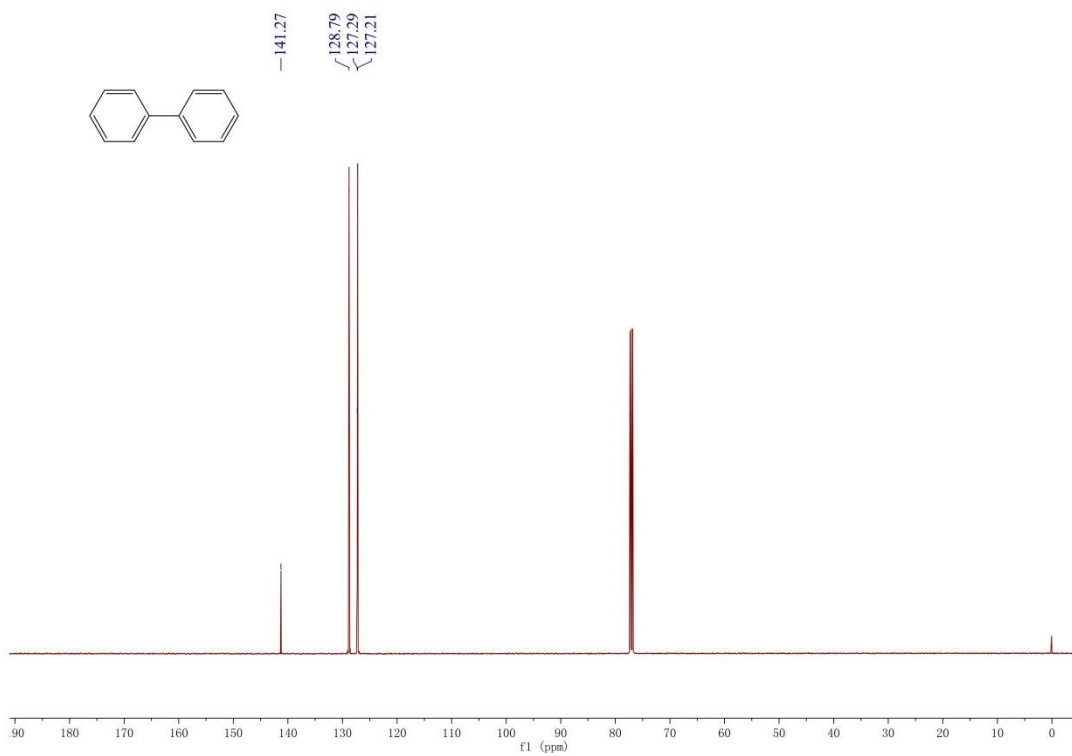


Spectra of Biphenyl

¹H-NMR

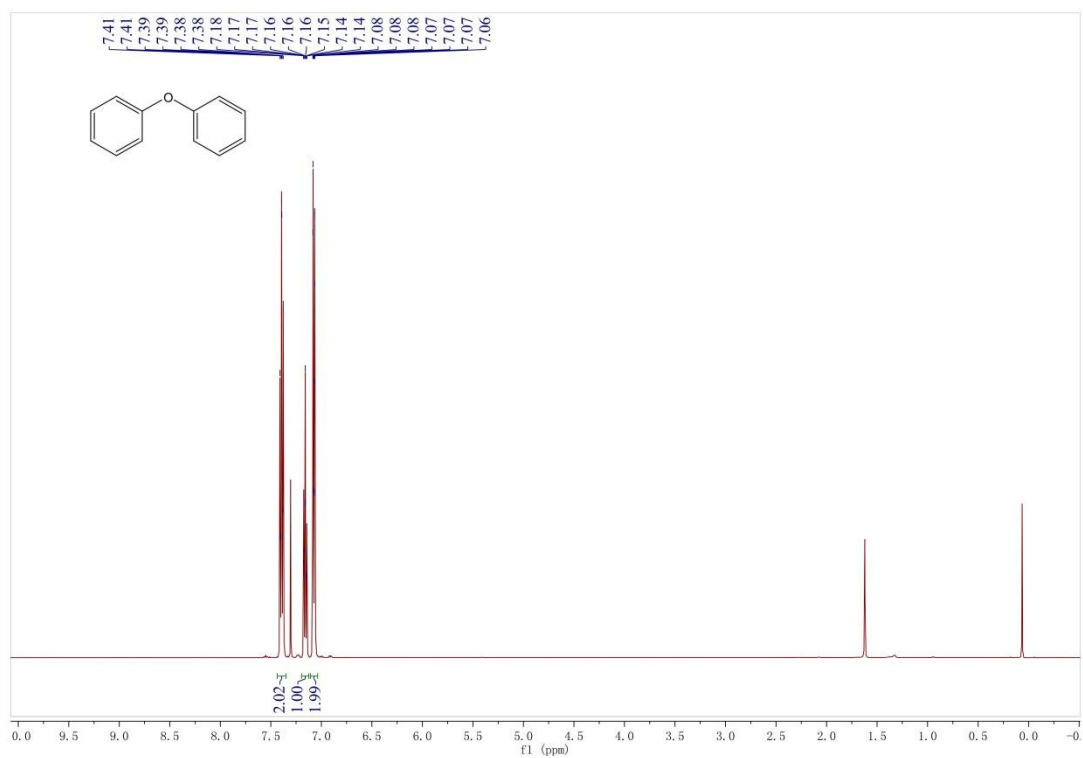


¹³C-NMR

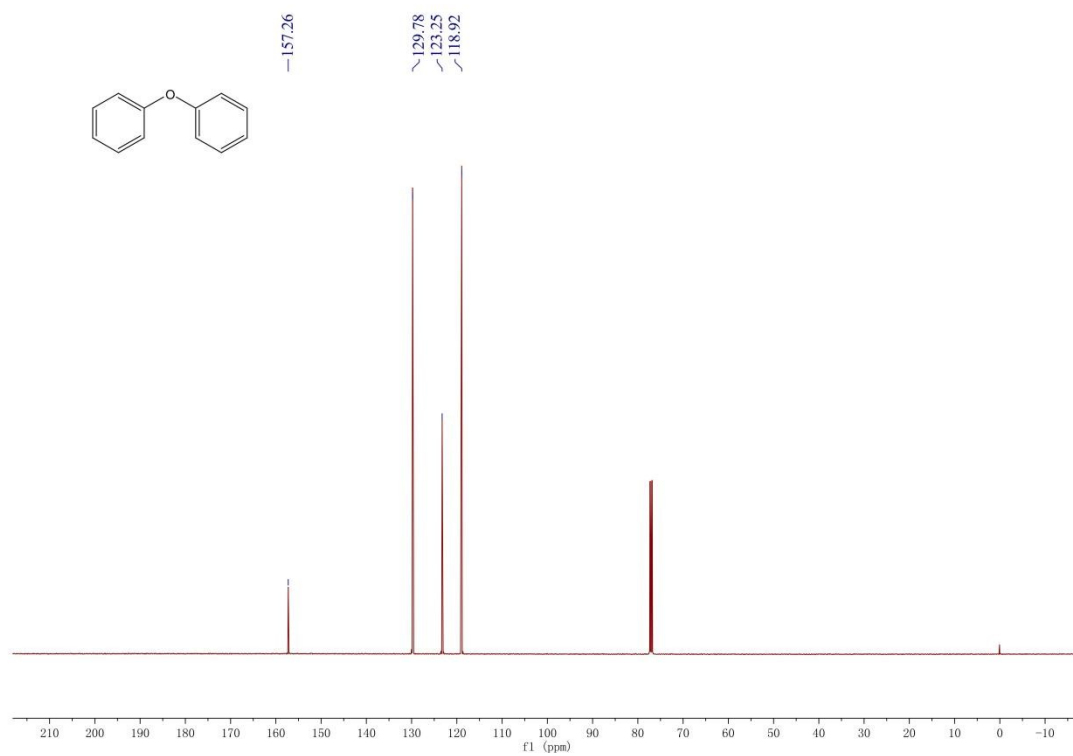


Spectra of Diphenyl ether

¹H-NMR

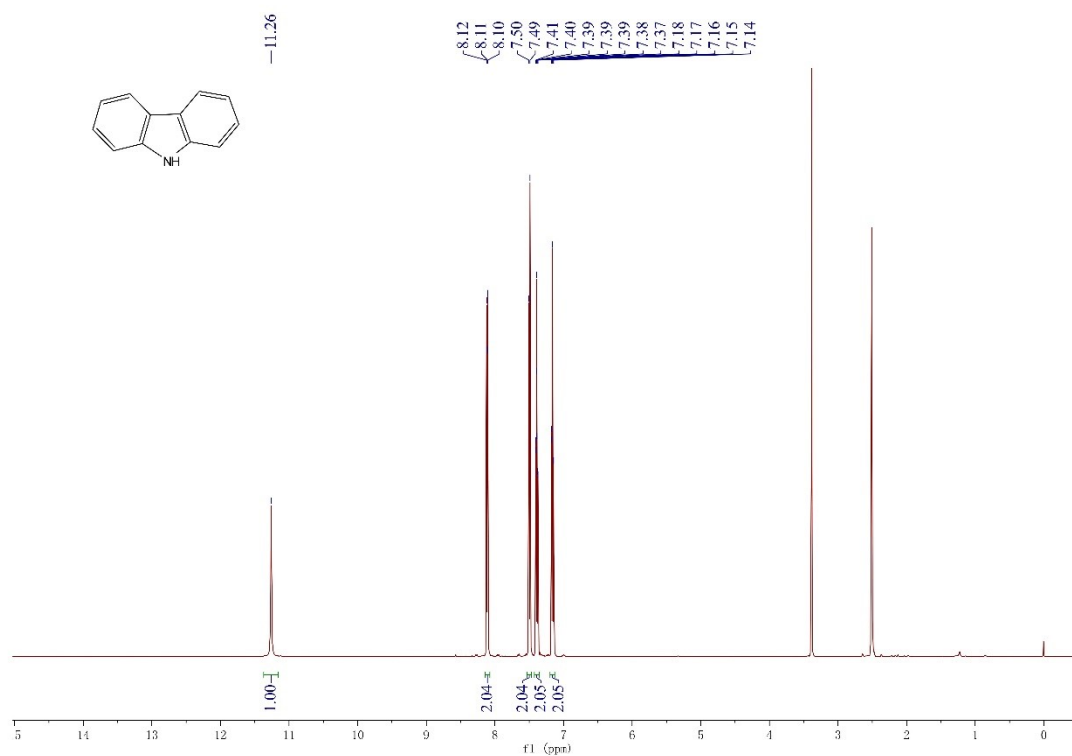


¹³C-NMR

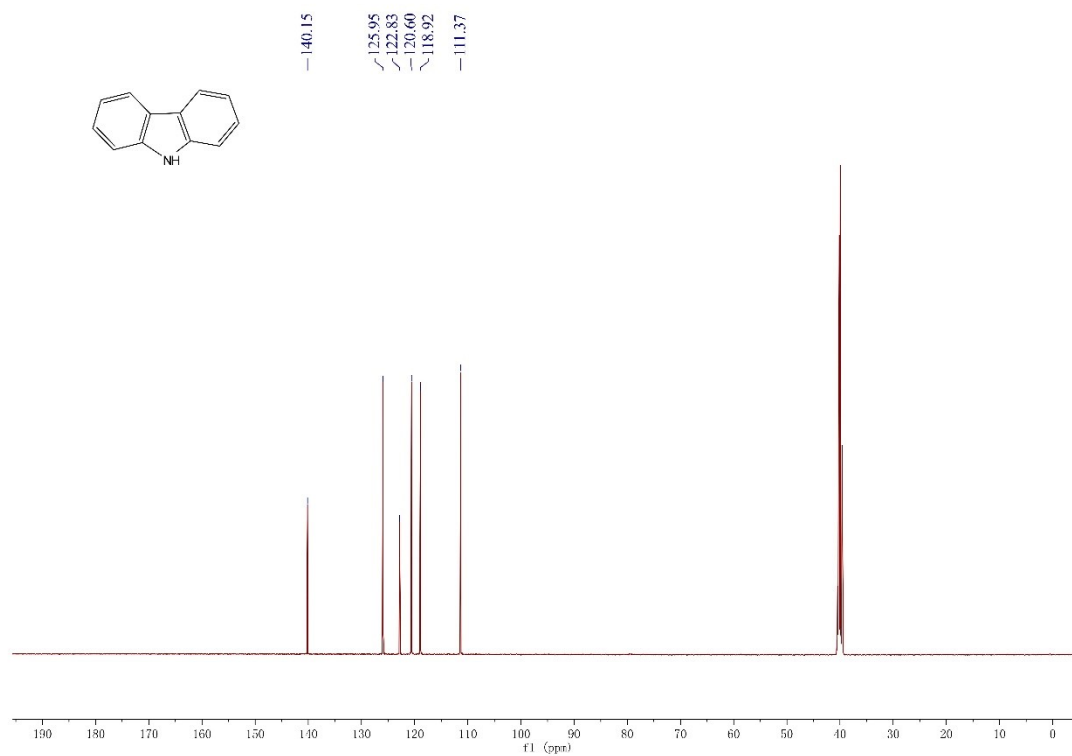


Spectra of Carbazole

¹H-NMR

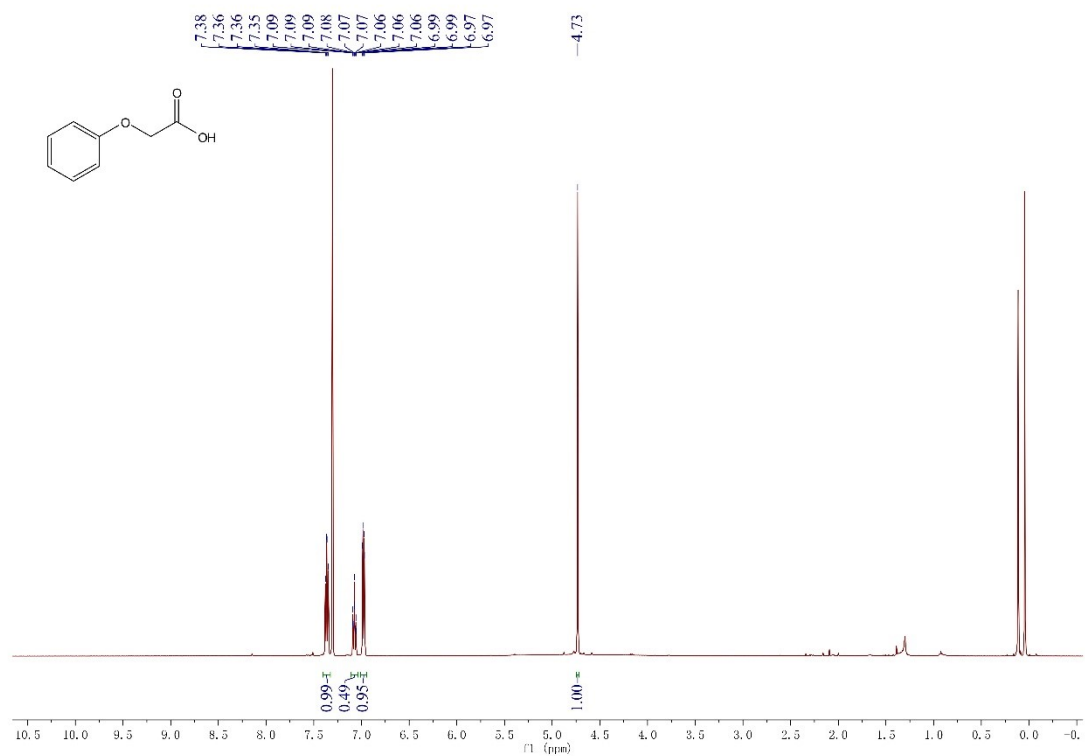


¹³C-NMR

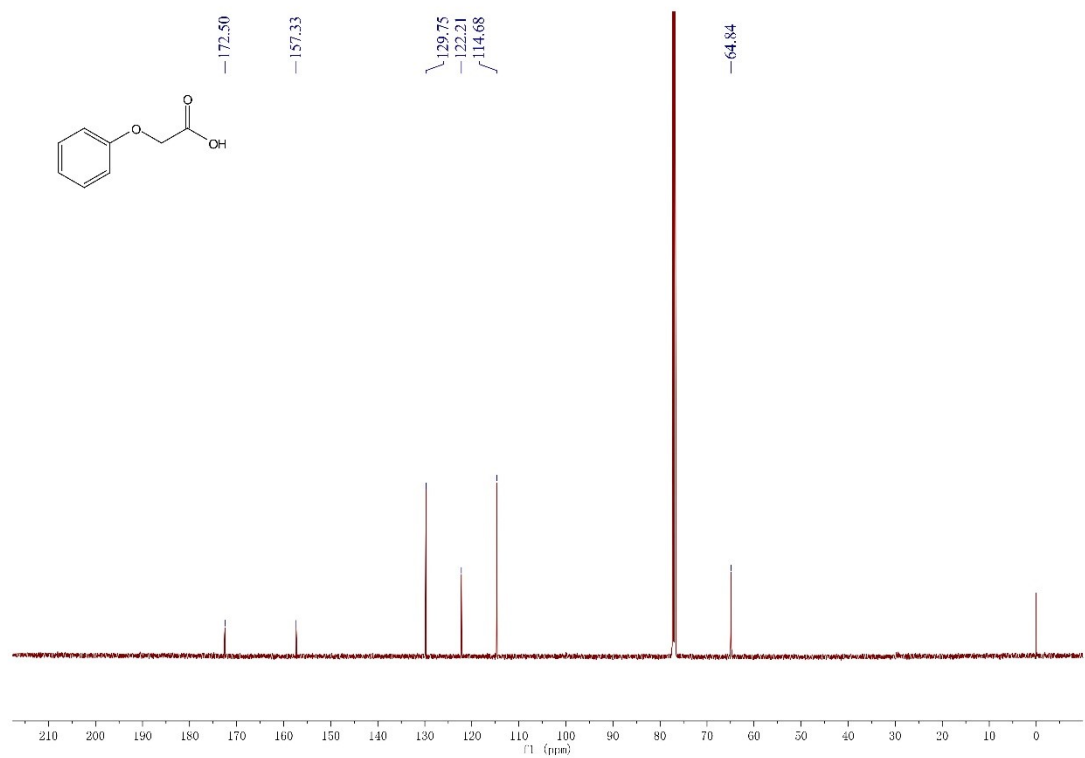


Spectra of Phenoxyacetic acid

$^1\text{H-NMR}$

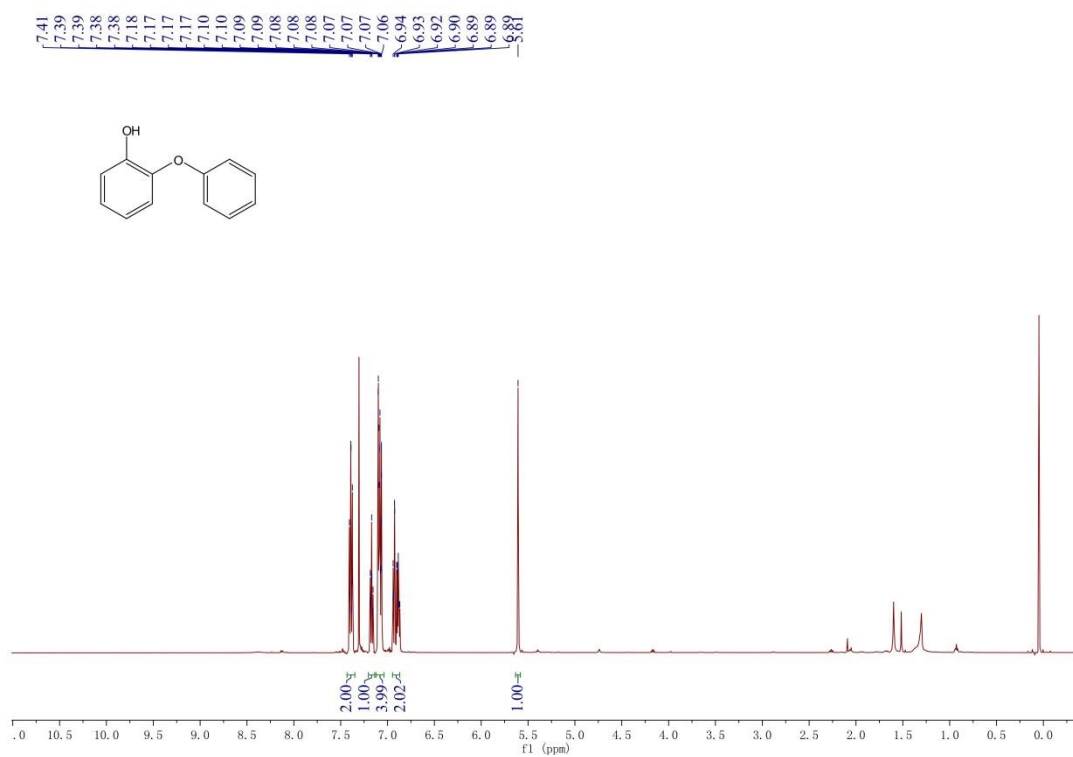


$^{13}\text{C-NMR}$



Spectra of 2-Phenoxyphenol

¹H-NMR



¹³C-NMR

